CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION

Diazinon and Chlorpyrifos Target Analysis:

Workplan Product for Development of Diazinon and Chrlorpyrifos Total Maximum Daily Loads in the Lower Sacramento River, Lower Feather River, Lower San Joaquin River, and the Main Channels of the Sacramento-San Joaquin River Delta

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 EXECUTIVE SUMMARY

This document summarizes the available data and existing criteria for chlorpyrifos and diazinon upon which to base numeric targets for development of Total Maximum Daily Loads for the Sacramento, Feather, and, San Joaquin Rivers, and the Sacramento-San Joaquin River Delta. The Sacramento and Feather Rivers are identified by the Central Valley Regional Water Quality Control Board (Regional Board) as impaired due to diazinon and are listed on the Federal Clean Water Act section 303(d) list of impaired water bodies. The San Joaquin River and the Sacramento-San Joaquin River Delta are identified as impaired due to chlorpyrifos and diazinon. A Total Maximum Daily Load must be developed for all listed water bodies and pollutants.

Numeric targets must protect the beneficial uses designated for the applicable water bodies, be consistent with state and Federal regulations, and be acceptable to the SWRCB and the U.S. EPA. The following alternative methods for developing a chlorpyrifos and diazinon numeric target are evaluated in this report: based on the State's anti-degradation policy, U.S. EPA water quality criteria development methodology, U.S. EPA water quality criteria methodology as used by California Department of Fish and Game (CDFG), Probabilistic Ecological Risk Assessment as used by Novartis Crop Protection, microcosm/mesocosm studies, and literature findings.

Regional Board staff has determined, based on currently available information, that an acceptable diazinon target would be between "zero" and the target derived by CDFG using U.S. EPA water quality criteria development methodology: 50 ng/L 4-day average and 80 ng/L 1-hour average. An acceptable chlorpyrifos target would be between "zero" and the target derived by CDFG: 14 ng/L 4-day average and 25 ng/L 1-hour average.

Establishment of final numeric targets and water quality objectives, however, will also depend on the evaluation of a number of factors. These factors include: the environmental characteristics of the watershed; water quality conditions that could be reasonably achieved through the coordinated control of all factors which affect water quality in the area; economic considerations; the need for developing housing in the region; and the need to develop and use recycled water (§13241; Porter-Cologne Water Quality Act).

Future scientific findings on the aquatic toxicity of diazinon or chlorpyrifos may also affect the numeric targets. In addition, the need to protect sensitive native or resident organisms, such as endangered species, may necessitate lower numeric targets.

Attainability of the targets, together with the other factors listed, will be evaluated as an implementation program for the TMDL is developed. Based solely on consideration of protection of beneficial uses and the information currently available to Board staff, it appears an acceptable target would be between "zero" and the diazinon and chlorpyrifos targets derived by the California Department of Fish and Game. These targets would apply only in the main stem rivers and main channels of the Delta.

2.0 ENVIRONMENTAL SETTING

The Central Valley consists of a structural downwarp that extends from Redding in the north to the Tehachapi Mountains in the south, more than 400 miles in length. The Sacramento Valley constitutes the northern third and the San Joaquin Valley the southern two-thirds of the Central Valley. Dissected uplands, river flood plains and channels, overflow lands and lake bottoms, and low alluvial plains and fans divide the Central Valley floor. Along the Valley's mountain borders, dissected uplands are underlain by structurally deformed unconsolidated to semi-consolidated continental deposits, of Pliocene and Pleistocene age. Uplands range from several hundred feet down to gently rolling lands. Alluvial plains and fans border the dissected uplands, are mostly flat with some gentle undulations and are underlain by undeformed to slightly deformed Pleistocene and Recent age alluvial deposits. Well-defined flood plains exist along major streams and rivers that are incised below the land surface. Flood plain and channel deposits are confined to stream channels and natural levees that slope away from the rivers in areas where rivers are surrounded by low-lying overflow lands (Bailey, 1966).

The Sacramento River watershed extends from the slopes of Mt. Shasta to the Sacramento-San Joaquin Delta and from the Coast Ranges east to the Sierra Nevada. The Sacramento River is 327 miles long and drains an area of about 27,000 square miles. The average surface water runoff from the Sacramento River yields 22 million acre-feet per year. The Lower Feather River is a tributary to the Sacramento River and flows approximately 60 miles from Oroville Dam, located three miles northeast of Oroville, to the Sacramento River at Verona, located 15 miles northwest of downtown Sacramento. The Lower Feather River watershed drains about 691 square miles of urban, agricultural, and undeveloped land. The Sacramento and Feather Rivers are impounded by dams above the Sacramento Valley border, which provide flood protection during winter, stored water for irrigation use during the spring and summer, and public water supply throughout the year (Bailey, 1966).

The Sacramento River basin has a variety of land uses, including urban, agriculture, and mining. More than two million acres of land in the Sacramento Valley are irrigated for agriculture. Major crops include rice, fruit, nuts, tomatoes, sugar beets, corn, alfalfa, and wheat (Domagalski and Brown, 1998). The average annual precipitation in the Sacramento Valley is approximately 36 inches; most of this rain falls during the months of November through March.

The San Joaquin River (SJR) watershed is bound by the Sierra Nevada Mountains on the east, the Coast Ranges on the west, the Delta to the north, and the Tulare Lake Basin to the south. From its source in the Sierra Nevada Mountains, the San Joaquin River flows southwesterly until it reaches Friant Dam. Below Friant Dam, the SJR flows westerly to the center of the San Joaquin Valley near Mendota, where it turns northwesterly to join the Sacramento River in the Delta. The main stem of the SJR has a length of about 300 miles and drains an area of about 13,500 square miles. The average unrestricted surface water runoff from the San Joaquin River yields approximately six million acre-feet per year. Most of this is diverted for use either within or outside the basin.

The major tributaries to the San Joaquin River are on the east side of the San Joaquin Valley, with drainage basins in the Sierra Nevada Mountains. Several smaller, ephemeral streams flow into the SJR from the west side of the valley. These streams have drainage basins in the Coast Range, flow intermittently, and contribute sparsely to water supplies. During the irrigation season, surface and subsurface agricultural return flows contribute greatly to these creeks and sloughs.

The San Joaquin Valley occupies approximately 18 million acres in the southern portion of California's Central Valley, accounting for almost 18 percent of the total land area of the state. The San Joaquin Valley is one of the most important agricultural areas in the United States. Most of the valley floor is agricultural land, and its agricultural history dates back to the 1870s. In addition to agriculture, the San Joaquin Valley is known for its high natural resource values. Precipitation is unevenly distributed throughout the San Joaquin River Basin; average annual precipitation in the San Joaquin Valley ranges from 8 inches in the south to 14 inches in the north; most of this rain falls during the months of November through April.

3.0 CHEMICAL PROPERTIES AND AQUATIC TOXICITY

3.1 Chemical Properties

The chemical properties of diazinon and chlorpyrifos determine their fate and transport in the environment, and their toxicity to aquatic organisms. Diazinon (chemical name: O, O-diethyl—O— [6-methyl-2-(1-methylethyl)-4-pirimidinyl] phosphorothioate) is sold under the trade names of Spectracide, Nipsan, Diagran, Dianon, Gardentox, and others. (Farm Chemicals Handbook, 2001). Diazinon is moderately soluble in water (60 parts per million [ppm] at 20^{o}C) and does not readily adsorb to soil organic matter (soil adsorption coefficient [Koc] 1007 to 1842), which means that it is likely to move off crops and soil in rainfall or irrigation runoff. Diazinon is moderately volatile (vapor pressure 0.64 millipascals [mPa] at 20^{o} C), indicating that diazinon can readily volatilize into air or fog, where it can be carried for some distance before returning to land or water in rainfall. Diazinon's hydrolysis rate constant is 0.005 per day at pH 7. (ARSUSDA, 1995). All of these chemical processes are influenced by pH, temperature and organic content. Diazinon's environmental fate is dominated by hydrolysis and microbial degradation (U.S. EPA, 1998).

Chlorpyrifos (chemical name: O, O-diethyl—O- (3,5,6-trichloro-2-pyridinyl) phosphorothioate) is sold under the trade names of Lorsban (agricultural use), Dursban (urban use), and others. (Farm Chemicals Handbook, 2001). Chlorpyrifos is relatively insoluble in water (0.73 ppm at 20^{o}C) and adsorbs strongly to soil organic matter (Koc 5300 to 14800), indicating that it is not likely to move off crops or soil. Chlorpyrifos is moderately volatile (vapor pressure 2.3 mPa at 20^{o} C), with a hydrolysis rate constant of 0.0236 per day at pH 7. (ARSUSDA, 1995). Like diazinon, the environmental fate of chlorpyrifos is also dominated by hydrolysis and microbial degradation. Degradation half-lives in soil and surface applications range from 33 to 56 and 7 to 10 days, respectively (Fountaine, 1987). Dissipation of chlorpyrifos from plant foliage is quite rapid, with dissipation half-lives of one week or less (Dow AgroSciences, 1998). In water, dissipation appears to result primarily from volatilization losses from the pond surface to pond sediments. Chlorpyrifos half-lives in pond sediment typically range from 14 to 64 days, with some longer times observed (Dow AgroSciences, 1998).

3.2 Aquatic Toxicity

Diazinon and chlorpyrifos are organophosphorus insecticides and their mode of action is inhibition of the enzyme cholinesterase, resulting in respiratory paralysis. Aquatic toxicity is generally considered in terms of acute or chronic effects. Acute toxicity is determined by exposing organisms to a test compound for a short time, usually 24 to 96 hours. Response is expressed as an effects concentration, $EC_{50,}$ or a lethal concentration, $LC_{50,}$ the concentration that produces the effect (such as lethality) in 50% of the individuals tested.

Chronic toxicity considers non-lethal endpoints, such as growth or reproductive effects, and test durations must be long enough to measure changes in one or more generations. A variety of measures are used to quantify chronic toxicity. A commonly accepted measure is the Maximum Acceptable Toxicant Concentration (MATC), which is the geometric mean of the No Observable Effects Concentration (NOEC) and the Lowest Observable Effects Concentration (LOEC) (Siepmann and Finlayson, 2000).

Acute Toxicity

Aquatic insects and crustaceans (invertebrates) tend to be particularly sensitive to diazinon and chlorpyrifos. Diazinon LC_{50}s typically range from 200 to 25,000 ng/L for aquatic invertebrates, and from 270,000 to 8,000,000 ng/L for fish. Chlorpyrifos LC_{50}s typically range from 60 to 800 ng/L for aquatic invertebrates, and from 3,000 to 800,000 ng/L for fish (Siepmann and Finlayson, 2000).

The cladoceran *Ceriodaphnia dubia* is one of the freshwater aquatic crustaceans most commonly used for toxicity testing. *C. dubia* LC_{50}s for diazinon and chlorpyrifos have been reported as 440 and 60 ng/L, respectively (Siepmann and Finlayson, 2000).

Chronic Toxicity

For diazinon, Siepmann and Finlayson (2000) report a *C. dubia* MATC of 340 ng/L. In another study, diazinon levels of 300 ng/L in a stream resulted in a 5 to 8 times decrease in mayfly and caddisfly emergence within three weeks of exposure; after twelve weeks, mayflies, damselflies, caddisflies, and amphipods were no longer detected in benthic samples (Arthur *et al*., 1983).

For chlorpyrifos, Siepmann and Finlayson (2000) report a *C. dubia* MATC of 40 ng/L. Chronic toxicity in invertebrates has been observed as reproductive inhibition in two sensitive species, *D. magna*, and a saltwater mysid, *Mysidopsis bahia*. Life cycle studies (21 to 35 days) report ranges of lowest-observed effect concentrations (LOECs) of 100 to 300 ng/L for *D. magna* and 4.0 to 10 ng/L for *M. bahia*.

Other types of sublethal effects, such as behavioral responses, have also been described (Scholz et al., 2000, Moore and Waring, 1996, and others). Behavioral bioassay endpoints have not generally been used as measures of toxic effect because data sets are limited and the significance of these behavioral responses is not well understood (Solomon et al., 2001). However, more subtle endpoints may become of interest as the science of toxicology advances and concern about ecological effects on sensitive or endangered species increases.

Additive Toxicity

Chemicals that have similar modes of action and toxicological effects, such as cholinesterase inhibition, are likely to exhibit additive toxicity (Bailey et al., 1997). Diazinon and chlorpyrifos, both cholinesterase inhibitors, are found concurrently in agricultural and urban runoff. Siepmann and Finlayson (2000) reviewed two studies on the joint toxicity of diazinon and chlorpyrifos to *C. dubia* (Bailey et al., 1997; CDFG, 1999) and concluded that the toxicities of chlorpyrifos and diazinon appear to be additive.

Using the cladoceran *C. dubia*, Bailey et al. (1997) added diazinon and chlorpyrifos separately and in combination to samples of laboratory and field water samples collected from a stream and a Sacramento residential stormwater outfall. Average 48-hour LC_{50} values in laboratory water were 400 ng/L (range 260-580 ng/ L) for diazinon and 66 ng/L (range 58-79 ng/ L) for chlorpyrifos. Chemical concentrations were measured and LC_{50} values were determined for diazinon-chlorpyrifos mixtures. Concentrations of diazinon and chlorpyrifos were converted to toxic units (1 toxic unit = LC_{50} of compound when tested alone). Levels of compounds expressed as toxic units were then compared directly to determine the contribution of each compound to the toxicity of the mixture.

If diazinon and chlorpyrifos exhibit additive toxicity, the LC_{50} value (expressed as toxic units) of the diazinon-chlorpyrifos mixture should be the sum of the respective fractions of diazinon and chlorpyrifos and should equal one. If toxicity were reduced by the combination, the LC_{50} of the mixture in toxic units would be less than one. If toxicity of one compound were augmented by the presence of other compound, the LC_{50} would be greater than one. LC_{50} values for the tests using diazinon and chlorpyrifos together were calculated for a total of 12 time intervals, and toxic units averaged 1.13. These data demonstrate that diazinon and chlorpyrifos exhibit additive toxicity when present together.

4.0 APPLICABLE STANDARDS

Section 303(c) of the Federal Clean Water Act requires States to adopt water quality standards to protect public health and enhance water quality. Water quality standards consist of designated uses of a water body and water quality criteria to protect these uses. Criteria are a level of water quality, expressed as either a numeric concentration or a narrative statement that will support a particular designated use. States are responsible for reviewing, establishing, and revising water quality standards. The Federal Clean Water Act requires states to submit all new or revised surface water quality standards to the U.S. EPA for approval. In the State of California, The State Water Resources Control Board (SWRCB) and the Regional Water Quality Control Boards (Regional Boards) are responsible for establishing and submitting water quality standards to U.S. EPA.

The State of California Porter-Cologne Water Quality Control Act defines water quality objectives (WQOs) as "*… the limits or levels of water quality constituents or characteristics which are established for the reasonable protection of beneficial uses of water or the prevention of nuisance within a specific area.*" State determined beneficial uses are equivalent to Federal designated uses. State WQOs are roughly equivalent to Federal water quality criteria. Combined State beneficial use designations and WQOs constitute Federal water quality standards.

WQOs are identified in the Water Quality Control Plan (Basin Plan) of each Regional Board. WQOs in a Basin Plan must conform to WQOs specified in statewide or regional policies and plans adopted by the SWRCB.

There are currently no numeric WQOs for diazinon or chlorpyrifos in the Sacramento or San Joaquin Rivers or the Sacramento-San Joaquin River Delta. The targets selected for this TMDL will be proposed as new water quality objectives as part of the TMDL implementation and Basin Plan Amendment process.

4.1 Beneficial Uses

The Water Quality Control Plan for the Sacramento-San Joaquin River Basins (Basin Plan)(CRWQCB—CVR, 1998) designates the following beneficial uses:

- Sacramento River: municipal and domestic supply, agricultural supply, industrial service supply, water-contact and non-water-contact recreation, cold and warm freshwater habitat, fish migration, fish spawning, wildlife habitat, and navigation.
- Lower Feather River: municipal and domestic supply, agricultural supply, water-contact recreation, canoeing, non-water-contact recreation, cold and warm freshwater habitat, fish migration, fish spawning, and wildlife habitat.
- Lower San Joaquin River: municipal and domestic supply, agricultural supply, industrial process and service supply, water-contact recreation, canoeing, non-water-contact recreation, warm freshwater habitat, fish migration, fish spawning, and wildlife habitat.
- Sacramento-San Joaquin Delta waterways: municipal and domestic supply, agricultural supply, industrial process and service supply, water-contact and non-water-contact recreation, warm and cold freshwater habitat, fish migration, warm water fish spawning, wildlife habitat and navigation.

The freshwater habitat use is likely the most sensitive use related to diazinon and chlorpyrifos concentrations. The definitions of the warm and cold freshwater habitat uses are similar: "*Uses of water that support warm (cold) water ecosystems including, but not limited to, preservation or enhancement of aquatic habitats, vegetation, fish, or wildlife, including invertebrates*."

4.2 Water Quality Objectives

The Basin Plan contains water quality objectives expressed as both narrative goals or numeric limits.

Narrative Water Quality Objective

The Basin Plan contains narrative water quality objectives for pesticides and toxicity; each is applicable to this pesticide TMDL. Following is the Basin Plan's narrative water quality objectives for pesticides:

· *No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses,*
· *Discharges shall not result in pesticide concentrations in bottom sediments or aquatic life that adversely affect beneficial uses,*
· *Pesticide concentrations shall not exceed those allowable by applicable antidegradation policies, and*
· *Pesticide concentrations shall not exceed the lowest levels technically and economically achievable*

The Basin Plan defines pesticides as: *"…any substance, or mixture of substances which is intended to be used for defoliating plants, regulating plant growth, or for preventing, destroying, repelling, or mitigating any pest, …or, any spray adjuvant; or, any breakdown products of these materials that threaten beneficial uses. Note that discharges of "inert" ingredients included in pesticide formulations must comply with all applicable water quality objectives."*

The Basin Plan's narrative water quality objective for toxicity specifies that "…*all waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life. This objective applies regardless of whether the toxicity is caused by a single substance or the interactive effect of multiple substances. Compliance with this objective will be determined by analyses of indicator organisms, species diversity, population density, growth anomalies, and biotoxicity tests of appropriate duration or other methods as specified by the Regional Water Board.*" This narrative objective applies to toxicity related to all pollutants, including pesticides.

The Regional Board must also consider applicable beneficial uses, Federal regulations governing the development of water quality criteria, and …"*all material and relevant information submitted by the discharger and other interested parties and numeric criteria and guidelines for toxic substances developed by the State Water Board, the California Office of Environmental Health Hazard Assessment, the California Department of Health Services, the US Food and Drug Administration, the National Academy of Sciences, the US Environmental protection Agency, and other appropriate organizations…"* (CRWQCB—CVR, 1998)

Policy with Respect to Maintaining High Quality Waters of Waters in California (Anti-degradation Policy)

In addition to the Basin Plan's narrative WQOs for pesticides and toxicity, the SWRCB's policy (Resolution 68-16) for maintaining high quality waters requires the maintenance of existing water quality, unless a change in water quality *"is consistent with maximum benefit to the people of the State; does not unreasonably affect present and anticipated beneficial uses; and, does not result in water quality less than that prescribed in water quality control plans or policies."* According to this policy, concentrations of diazinon and chlorpyrifos should not be allowed to increase above natural background levels (see discussion in the Basin Plan under "Policy for Application of Water Quality Objectives" (CRWQCB-CVR, 1998, pg. IV-16.00)). For diazinon and chlorpyrifos the water quality upstream of all discharges is essentially "zero". Detectable levels of diazinon and chlorpyrifos could only be allowed if the above conditions are met.

Numeric Water Quality Objective

Currently, the Basin Plan does not specify any numeric WQOs for diazinon or chlorpyrifos. In developing numerical water quality objectives to use as TMDL targets, careful consideration will need to be given to assure that existing State and Federal policies and regulations (including the Basin Plan narrative toxicity objective and anti-degradation provisions) are met. The Basin Plan contains a "Policy for Application of Water Quality Objectives" (CRWQCB-CVR, 1998) that explains how to interpret the narrative toxicity objective. Federal regulations require that any criteria or WQO established by the State be based on "…(i) 304(a) Guidance; or (ii) 304(a) Guidance modified to reflect site-specific conditions; or (iii) other scientifically defensible methods" (40 CFR § 131.11 (b) et seq.). No matter which scientific method is used, the criteria or water quality objective must be established at a level "…sufficient to protect the designated use." (40 CFR § 131.11(a)(2)

Additive Toxicity

When a water body contains more than one pesticide, the Basin Plan requires that cumulative impacts be considered. In the absence of information suggesting otherwise, it must be assumed that chemicals with similar toxicological effects will exhibit additive toxicity. Diazinon and chlorpyrifos have the same toxicologic mode of action--inhibition of the enzyme cholinesterase, resulting in respiratory paralysis. The Basin Plan specifies that the additive toxicity may be quantified by summing the concentration of each chemical, divided by its toxicologic limit as follows:

$$\sum_{i=1}^{n} \frac{[\text{concentration of toxic substance}]_i}{[\text{toxicologic limit for substance in water}]_i} \geq 1.0$$

where n is the number of toxic substances. A sum equal to or greater than one indicates toxicological risk, and a potential impact to beneficial uses.

As part of the process to develop a program of implementation to meet the water quality objectives for diazinon and chlorpyrifos, the Regional Board will also consider the additive effects of those two chemicals. This may result in the establishment of load limits or reductions in concentrations below the individual water quality objectives in those instances where diazinon and chlorpyrifos co-occur in the environment.

4.3 Water Quality Objectives Versus Numeric Targets

As discussed earlier, numeric WQOs for diazinon or chlorpyrifos do not currently exist. Establishing numeric WQOs must be first step in the TMDL process. All objectives must protect beneficial uses and must comply with all State and Federal policies and regulations. The Regional Board may also adopt interim numeric targets that could be used to indicate progress toward achieving WQOs, or targets that help correlate implementation actions to attainment of water quality objectives, such as targets for specific sources, or for mass loading.

A strict interpretation of the SWRCB's anti-degradation policy could result in a target of only natural background concentrations of diazinon and chlorpyrifos, which would be "none detected". To establish a target above "none detected", the Regional Board would need to make a determination that a higher level is to the maximum benefit of the people of the state. Such determinations are frequently made for point source discharges, and it is generally recognized that some degradation of water quality is permissible, as long as beneficial uses are protected.

Therefore, the selection of numeric targets for diazinon and chlorpyrifos must be based on fully protecting beneficial uses while allowing some level of these pesticides to be present. The mandates to protect aquatic habitat and not allow detrimental physiological responses still apply, however, as does the necessity to comply with Federal and state requirements. The Regional Board will rely on currently available information to select numeric targets for diazinon and chlorpyrifos, including existing water quality criteria, risk assessment calculations, and toxicity tests.

5.0 NUMERIC TARGET

The targets selected for this TMDL will be proposed as new water quality objectives as part of the TMDL implementation process. The process will begin with a Basin Plan Amendment public hearing by the Regional Board. Any proposed target adopted by the Board must be consistent with State and Federal regulations, and be approvable, as a water quality objective, by the SWRCB, the Office of Administrative Law and the U.S. EPA. Various methods of deriving a numeric target are considered here followed by an evaluation of the methods and their suitability as an approvable water quality objective.

5.1 Geographic Areas Where Target Applies

The numeric target described in this document apply to the following areas:

- The lower Sacramento River south of the Colusa Basin Drain to the "I" Street Bridge
- The lower Feather River from the fish barrier dam to the confluence with the Sacramento River
- The lower San Joaquin River downstream of the Mendota dam to the Airport Way Bridge near Vernalis
- The main channels of the Sacramento-San Joaquin River Delta within the geographic boundaries of the Delta as listed in Water Code Section 12220; separate targets and water quality objectives may be adopted for Delta sloughs and creeks that have little tidal interchange or natural flow.

5.2 Methods Used to Derive a Numeric Target

The Regional Board will rely on currently available information to select numeric targets for diazinon and chlorpyrifos, including existing water quality criteria and results from risk assessments and toxicity tests. As previously stated, numeric targets must protect the beneficial uses designated for the applicable water bodies, be consistent with state and Federal regulations, and be acceptable to the SWRCB and the U.S. EPA. This section examines the approaches that are being considered for use in deriving numeric targets for diazinon and chlorpyrifos:

- Anti-degradation policy
- U.S. EPA Water Quality Criteria development methodology
- U.S. EPA Water Quality Criteria methodology as used by California Department of Fish and Game (CDFG)
- Probabilistic Ecological Risk Assessment (PERA) as used by Novartis Crop Protection
- Microcosm/mesocosm studies
- Literature Findings

Anti-degradation Policy

Numeric Targets based on the anti-degradation policy would not allow pesticide concentrations to exceed natural "background" levels, i.e., none detected, or "zero". Exceptions would be allowed if the Regional Board finds that allowing higher concentrations is in the State's best interest. However, the protection of Beneficial Uses and consistency with other State and Federal policies must still be maintained.

U.S. EPA Water Quality Criteria Methodology

U.S. EPA guidelines (Stephan et. al, 1985) for deriving numeric water quality criteria (WQC) for aquatic organisms provide a method to review available toxicity data for a water quality constituent and to mathematically derive two values--the criterion maximum concentration (CMC), an acute criterion, and the criterion continuous concentration (CCC), a chronic criterion. According to the guidelines, restricting concentrations to levels at or below these criteria should provide aquatic organisms with a "reasonable level" of protection and prevent "unacceptable" impacts.

U.S. EPA water quality criteria are intended to protect all species for which acceptable toxicity data exist, and species for which those in the data set serve as surrogates (P. Woods, personal communication). The criteria are met if the one-hour average concentration of the constituent does not exceed the acute criterion and the four-day average concentration does not exceed the chronic criterion more than once every three years at a given location.

Acute toxicity data from acceptable tests on freshwater and saltwater organisms are used to determine a Final Acute Value (FAV). U.S. EPA guidelines (Stephan et. al. 1985) require eight families of freshwater organisms for which data should be available for deriving a freshwater FAV, and eight families of saltwater organisms for deriving a saltwater FAV, including:

- Salmonidae (e.g., chinook salmon, rainbow trout)
- a second fish family, preferably one including commercial or recreational species (e.g. bluegill, catfish)
- a third family of vertebrates (e.g. fish, amphibian)
- a planktonic crustacean (e.g., daphnid, copepods)
- a benthic (bottom-dwelling) crustacean (e.g., crayfish)
- an aquatic insect invertebrate
- a family from a group that is not an arthropod or vertebrate (e.g., mollusks)
- another taxonomic group not already represented

The FAV is calculated using the selected GMAVs and cumulative probabilities (P), as follows:

$$S^2 = \frac{\sum((\ln GMAV)^2) - \frac{(\sum(\ln GMAV))^2}{4}}{\sum(P) - \frac{((\sum(\sqrt{P}))^2}{4}}$$

$$L = \frac{\Sigma(\ln GMAV) - S \cdot \Sigma(\sqrt{P})}{4}$$

$$A = S(\sqrt{0.05}) + L$$

$$FAV = e^{A}$$

where:

- the Genus Mean Acute Value (GMAV) is the geometric mean of all SMAVs for each genus
- the GMAVs are ranked (R) from "1" for the lowest to "N" for the highest; identical GMAVs are arbitrarily assigned successive ranks
- the cumulative probability (P) is calculated for each GMAV as R/(N+1)
- the four GMAVs with cumulative probabilities closest to 0.05 are selected; if fewer than 59 GMAVs are available, these will always be the four lowest GMAVs

The equation generates a more conservative (i.e. lower) FAV as the number of GMAVs decrease; this mitigates the uncertainties associated with small data sets. If data are not available from all eight taxonomic groups, the criteria cannot be developed unless there is a specific rationale for making an exception. The Species Mean Acute Value (SMAV) is the geometric mean of EC_{50} values and LC_{50} values from all accepted toxicity tests performed on that species.

Chronic toxicity data from acceptable tests on freshwater and saltwater organisms are used to determine a Final Chronic Value (FCV). If data are available for the eight families, the FCV is calculated using the same procedure as described for the FAV. If sufficient data are not available, the following formula is used:

$$FCV = \frac{FAV}{FACR}$$

where

- Chronic values are obtained by calculating the geometric mean of the NOEC and the LOEC values from accepted chronic toxicity tests
- Acute-Chronic Ratios (ACR) are calculated for each chronic value for which at least one corresponding acute value is available; whenever possible, the acute test(s) should be part of the same study as the chronic test
- The Final ACR (FACR) is calculated as the geometric mean of all the species mean ACRs available for both freshwater and saltwater species

Plant toxicity data from algae or aquatic vascular plants are used to determine a Final Plant Value (FPV). The FPV is the lowest result from a test with a biologically important endpoint.

U.S. EPA guidelines specify that a WQC consists of two concentrations, the Criterion Maximum Concentration (CMC), and the Criterion Continuous Concentration (CCC). The CMC is one-half the FAV. The CCC is the lowest of three values: the FCV, the FPV, or the Final Residue Value (FRV). The FRV is intended to prevent pesticide concentrations in commercially or recreationally important species from affecting marketability because applicable action levels are exceeded, and to protect wildlife that consume aquatic organisms. The WQC can be lowered to protect important resident species (Stephan et al., 1985).

U.S. EPA Criteria for Diazinon

In 1986 the U.S. EPA published draft freshwater quality criteria for diazinon (U.S. EPA, 1998) using the guidelines described above. Acceptable acute toxicity data were available for twelve invertebrate and ten fish species. Eight of the twelve invertebrates were the most sensitive organisms tested. Freshwater fish demonstrated only moderate sensitivity to diazinon. The four lowest GMAVs for freshwater organisms (Table 1) were used to calculate the FAV. The FAV for diazinon was 183 ng/L, and the draft acute criterion was one-half of that value, 90 ng/L. This draft value is an order of magnitude greater than the U.S. EPA's previous instantaneous maximum value for diazinon of 9.0 ng/l, and may change again when the U.S. EPA criteria development for diazinon is completed.

Table 1. Four Lowest Genus Mean Acute Values of Freshwater Animals Exposed to Diazinon (U.S. EPA, 1998)

Rank	Genus	GMAV (ng/L)
1	*Gammarus* Species: *G. fasciatus;* Amphipod	200
2	*Ceriodaphnia* Species: *C. dubia;* Cladoceran	377
3	*Daphnia* Species: *D. pulex; D. magna;* Cladoceran	812
4	*Simocephalus* Species: *S. serrulatus;* Cladoceran	1,590

Seven chronic toxicity values for six species of freshwater organisms were evaluated. Due to insufficient chronic toxicity data, ACRs were calculated for certain species only. However, the ratios varied so dramatically that a final ACR could not be calculated following U.S. EPA guidelines. Therefore, the draft U.S. EPA diazinon criteria document does not propose chronic diazinon criterion. A chronic value for diazinon may be included in the final version of the document.

U.S. EPA Criteria for Chlorpyrifos

In 1998 the U.S. EPA published draft freshwater quality criteria for chlorpyrifos (U.S. EPA, 1986) using the guidelines described above. Acceptable freshwater acute toxicity data were available for seven fish species and eleven invertebrate species. The nine most sensitive species were invertebrates. Acute toxicity values for the four most sensitive genera, all invertebrates, were within a factor of four (Table 2), and the SMAVs within each genera were within a factor of three. The freshwater FAV for chlorpyrifos was 167 ng/L; the acute criterion was 83 ng/L.

Table 2. Four Lowest Genus Mean Acute Values for Freshwater Animals Exposed to Chlorpyrifos (U.S. EPA, 1986)

Rank	Genus	GMAV (ng/L)
1	Gammarus *Amphipod* Species: *G. fasciatus, lacustris, pseudolimnaeus*	185
2	*Pteronarcella* Stonefly Species: *P. badia*	380
3	*Claassenia* Stonefly Species: *C. sabulosa*	570
4	*Leptoceridae* Trichoptera Species: *L. sp.*	770

Acceptable saltwater acute toxicity data were available for five species of invertebrates and ten species of fish. Acute values ranged from 35 ng/L for the mysid, *Mysidopsis bahia*, to 1,991,000 ng/L for larvae of the eastern oyster, *Crassostrea virginica*. Four of the five invertebrate species were arthropods, and all four were more sensitive than the fish species tested. The saltwater FAV was 23 ng/L, which was lower than the lowest GMAV. The saltwater acute criterion was one half the FAV, or 11 ng/L

Acceptable chronic toxicity data for chlorpyrifos were available for only one freshwater species, the fathead minnow, *Pimephales promelas*, and the freshwater ACR was greater than 1,417 ng/L. Acceptable chronic toxicity data for seven saltwater species were available: the mysid, *M. bahia*, and six fishes. The Species Mean ACRs for the seven saltwater species ranged from 1,374 to 228,500 ng/L, although the ACRs for the five most sensitive species only ranged from 1.4 to 12.5. Therefore, the geometric mean of these five saltwater species, 4, was used as the Final ACR for chlorpyrifos. Division of the freshwater and saltwater FAVs by the Final FACR of 4 resulted in freshwater and saltwater chronic criteria of 41 and 5.6 ng/L, respectively. (U.S. EPA, 1986)

California Department of Fish and Game Criteria for Diazinon

In 2000 the California Department of Fish and Game (CDFG) published freshwater quality criteria for diazinon, and fresh and saltwater criteria for chlorpyrifos (Siepmann and Finlayson, 2000), using the U.S. EPA guidelines described above (Stephan et al., 1985).

Forty acceptable acute toxicity values were available to calculate a freshwater FAV for diazinon. All eight families specified by U.S. EPA (Stephan et al., 1985) were represented. The four lowest GMAVs for freshwater organisms used to calculate the FAV are presented in Table 3. The FAV for diazinon was 160 ng/L. Based upon U.S.

EPA guidelines, a CMC is calculated as one-half of the final acute value, and the CDFG CMC for diazinon was 80 ng/L.

Table 3. Four Lowest Genus Mean Acute Values of Freshwater Animals for Diazinon (Siepmann and Finlayson, 2000)

Rank	Genus	GMAV (ng/L)
1	*Gammarus* Species: *G. fasciatus;* Amphipod	200
2	*Ceriodaphnia* Species: *C. dubia;* Cladoceran	440
3	*Daphnia* Species: *D. pulex, D. magna;* Cladoceran	1,060
4	*Simocephalus* Species: *S. serrulatus;* Cladoceran	1,590

Five ACRs for four species were available to calculate a FCV for diazinon. As required by U.S.EPA (Stephan et al., 1985), these included a fish (fathead minnow), an invertebrate (mysid), and an acutely sensitive freshwater species (cladoceran). U.S. EPA guidelines (Stephan et al., 1985) specify that in cases where acute-chronic ratio (ACR) values increase with increasing LC_{50} values, only ACR values for species with SMAVs close to the FAV should be used to calculate the final ACR. This was the case with diazinon; ACR values for only the three acutely sensitive species (*C. dubia*, *D. magna*, and *M. bahia*) were used to calculate the final ACR. The final ACR was 3. The FCV, and thus the chronic criterion, was 50 ng/L. Insufficient data were available to calculate acute or chronic saltwater WQC for diazinon.

California Department of Fish and Game Criteria for Chlorpyrifos

Forty-three acceptable acute toxicity values were available to calculate a freshwater FAV for chlorpyrifos. All eight families specified by U.S. EPA (Stephan et al., 1985) were represented. The four lowest GMAVs for freshwater organisms used to calculate the FAV are presented in Table 4. The freshwater FAV for chlorpyrifos was 50 ng/L. Based upon U.S. EPA guidelines, a criterion maximum concentration is calculated as one-half the FAV; therefore, the CDFG freshwater WQC for chlorpyrifos was 25 ng/L.

Table 4. Four Lowest Genus Mean Acute Values of Freshwater Animals for Chlorpyrifos (Siepmann and Finlayson, 2000)

Rank	Genus	GMAV (ng/L)
1	Ceriodaphnia Species: *C. dubia*; Cladoceran	60
2	*Gammarus* Species: *G. lacustris;* Amphipod	110
3	Neomysis Species: *N. mercedis*; Mysid	150
4	*Petronarcella* Species: *P. badia* Stonefly	380

Forty acceptable acute toxicity values were available to calculate a saltwater FAV for chlorpyrifos. All eight families specified by U.S. EPA (Stephan et al., 1985) were represented. The four lowest GMAVs for freshwater organisms used to calculate the FAV are presented in Table 5. The saltwater FAV for chlorpyrifos was 30 ng/L. Based upon U.S. EPA guidelines, a criterion maximum concentration is calculated as one-half of the FAV; therefore, the CDFG saltwater WQC for chlorpyrifos was 15 ng/L.

Table 5. Four Lowest Genus Mean Acute Values of Saltwater Animals for Chlorpyrifos (Siepmann and Finlayson, 2000)

Rank	Genus	GMAV (ng/L)
1	Mysidopsis Species: *M.bahia*; Mysid	40
2	*Penaeus* Species: *P. aztecus, P. duorarum;* Shrimp	690
3	Leuresthes Species: *L. tenuis*; California Grunion	1,200
4	*Palaemonetes* Species: *P. pugio;* Grass Shrimp	1,500

Eight acceptable paired acute and chronic toxicity tests were available for deriving an ACR for chlorpyrifos. Only two of those ACRs were used to calculate a final ACR for chlorpyrifos because U.S. EPA (Stephan et al., 1985) guidelines specify that if ACR values increase or decrease as the SMAVs increase, as the ACR values generally do with chlorpyrifos, only species with SMAVs close to the FAV should be used to calculate the final ACR. Therefore, the FACR for chlorpyrifos is the geometric mean of the ACRs for *C. dubia* and *M. bahia*. The FACR was 3.5. The freshwater FCV was 14 ng/L and the saltwater FCV was 9.0 ng/L.

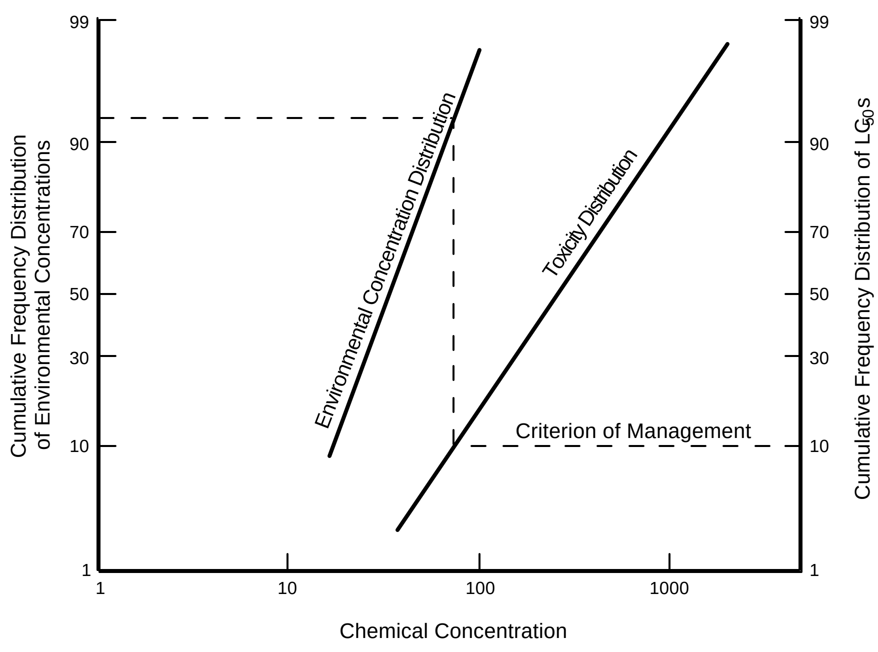
Probabilistic Ecological Risk Assessment

The Probabilistic Ecological Risk Assessment (PERA) methodology uses distributions of measured concentrations in a water body and concentrations associated with a specific toxicologic benchmark determined in laboratory tests, such as the LC_{50}. The data for each distribution are ranked from lowest to highest and summed to derive cumulative frequencies of occurrence. The cumulative frequencies are then plotted on logarithmic probability scales. (Figure 1)

The cumulative distribution of measured concentrations indicates the probability that a particular concentration will be exceeded in the water body. The cumulative distribution of toxicity data indicates the probability that a specific toxicological benchmark will be exceeded. The degree of overlap of these two plots indicates the joint probability of exposure and toxicity. This percentile and the toxicity distribution are used to determine the chemical concentration associated with this level of toxic effect. The resulting concentration and the environmental concentration distribution are used to determine the percent of time that this level of impact is not expected to occur. The “Criterion of Management” is the percent of species for which the toxic effect is deemed acceptable.

PERA generally uses LC_{50} values because the largest number of data points are available for that endpoint, and, therefore, its distribution has the highest confidence. The combination of percent lethality and percent of time determine the level of toxicity to aquatic life. Selection of an acceptable level of toxicity must consider community resilience and redundance of function within the ecosystem (Marshack, 2000).

Figure 1. Probabilistic Ecological Risk Assessment Method



<u>Probabilistic Ecological Risk Assessment of Diazinon in the Sacramento-San Joaquin River System</u>

Giddings et al. (2000) conducted a probabilistic ecological risk assessment for diazinon in the Sacramento-San Joaquin River system. The study used acute toxicity data (EC_{50}s and LC_{50}s) from three sources: the U.S. EPA's pesticide toxicity database for diazinon (U.S. EPA, 1995), a diazinon hazard assessment prepared by the California Department of Fish and Game (Menconi and Cox, 1994), and the U.S. EPA's AQUIRE database (U.S.

EPA, 1995). The U.S. EPA toxicity database contained data for 19 species (32 values) evaluated for product registration. The CDFG hazard assessment used data for 19 species (33 values) to derive a freshwater water quality criterion for protection of aquatic species. AQUIRE provided acute toxicity data for 57 species (112 values). Although the studies overlapped considerably, data were available for a total of 63 different species, approximately half of which were arthropods.

The study used data on concentrations of diazinon in the San Joaquin and Sacramento Rivers and their tributaries, including agriculturally dominated creeks and irrigation channels, for 1991 to 1994 from the US Geological Survey (MacCoy et al., 1995), the California Regional Water Quality Control Board – Central Valley Region (Foe, 1995), and the California Department of Pesticide Regulation (Ross, 1991, 1992a, 1992b, 1993a, 1993b, 1993c). These are the primary agencies responsible for collecting and assessing pesticide water quality data.

The 5th and 10th percentiles of the LC50 values for arthropods were 195 and 483 ng/L, respectively. The 5th and 10th percentiles of the LC50 values for all species were 1,117 and 3,710 ng/ L, respectively. The authors conclude that, based on the available exposure and toxicity data, diazinon does not present a direct ecological risk to fish populations in the Sacramento-San Joaquin River system, nor to most of the important invertebrates. Diazinon concentrations exceeded the toxic level for the most sensitive 10% of arthropod species (primarily cladocerans) during January and February at some locations, especially in the agricultural drains flowing into the San Joaquin River. Indirect effects on fish may occur if sensitive arthropods are reduced at critical periods when they are needed as food by early life stages of fish. However, the authors' PERA analysis indicates such effects on fish are unlikely because the most sensitive invertebrates are not major food sources for the nine fish species of concern in the Sacramento-San Joaquin system.

The authors provide six specific conclusions from their PERA risk assessment:

- Fish in the Sacramento-San Joaquin River system are unlikely to be at risk of acute effects from diazinon
- Fish are unlikely to be at risk of direct chronic effects from diazinon
- Sensitive arthropods are occasionally exposed to toxic levels of diazinon in the mainstem,
- but toxic exposures occur more frequently in the drains
- The highest probability of toxic effects on sensitive arthropods occurs in January and February
- Cladocerans are by far the most sensitive arthropods to diazinon, and are at the greatest risk
- Cladocerans are not the primary food source for any of the fish species of concern, and fish are unlikely to be affected by reductions in populations of sensitive arthropods

Microcosms and Mesocosms

Microcosms and mesocosms are small-scale and medium-scale experimental ecosystems used to study the fate and effects of chemicals under quasi-natural conditions. Microcosm and mesocosm studies are typically included in the later stages ("upper tiers") of a chemical risk assessment to confirm and extend the results of simpler, more highly controlled laboratory studies such as standard toxicity tests. Because they more closely simulate natural ecosystems, microcosms and mesocosms are generally more variable, and experimental results are less repeatable, than most laboratory tests. However, these systems can provide valuable information that cannot be obtained easily (or at all) from simpler studies. Specifically, microcosms and mesocosms:

- usually contain diverse communities of microorganisms, plants, zooplankton, benthic invertebrates, and fish, allowing simultaneous measurement of chemical effects on a wide variety of taxonomic groups
- incorporate mechanisms of ecological recovery from chemical stress, such as replacement of chemical-sensitive species by more tolerant species, although to a lesser extent than in open natural ecosystems
- allow for exposure regimes (including frequency and duration of exposure, and partitioning between sediment and water) that are more realistic than typical laboratory studies

<u>Application of Microcosms and Mesocosms</u>

Giddings et al. (1996) and Giddings (1992) conducted studies on diazinon in large outdoor microcosms and pond mesocosms. The objectives of the studies were to measure the effects of season-long exposures from agricultural runoff and spray drift, and to determine the relationship between diazinon exposure level and effects. Effects were measured on major taxonomic groups including phytoplankton, periphyton, macrophytes, zooplankton (cladocerans, copepods, and rotifers), benthic invertebrates (mainly immature insects including chironomids, mayflies, caddisflies, and damselflies), and fish.

The microcosms were established in 11.2-m^3 fiberglass tanks, using water and sediment from uncontaminated ponds, and were stocked with juvenile bluegill sunfish (*Lepomis macrochirus*). Eight loading rates were used, with two microcosms at each concentration, plus two controls. The treatment regimes (applied three times at 7-day intervals) resulted in exposure concentrations ranging from 5,100 to 914,000 ng/l (96-hour maxima). Seventy-day time-weighted averages ranged from 2,400 to 443,000 ng/l.

The mesocosms were 0.1-acre (0.025-hectare) earthen ponds containing sediment and water from the same sources as the microcosms, and were stocked with adult bluegill sunfish. Five treatment levels plus controls were used in the mesocosm study, with four ponds at each of the two lowest levels and the controls, and three ponds at the three highest levels. The ponds were treated six times with diazinon, alternating between spray applications (simulating off-target drift) and direct aqueous applications (simulating surface runoff). The mesocosm treatment regimes created 96-hour maximum concentrations ranging from 2,300 to 28,000 ng/l.

Abundances of phytoplankton, periphyton, macrophytes, zooplankton, benthic macroinvertebrates, and emergent insects were monitored in both studies. Fish growth and survival were measured in the microcosm study, and fish reproduction, growth and survival were measured in the mesocosm study.

Cladocerans were severely reduced at all diazinon treatment levels in both microcosms and mesocosms. Copepods and rotifers were less sensitive, with effects first occurring at exposure levels in the 8,000–28,000 ng/l range. Among the insects, caddisflies (Trichoptera) and some groups of midges (Ceratopogonidae and Pentaneurini) were affected at the lowest levels (2,000–5,000 ng/l). Mayflies (Ephemeroptera) and several groups of midges were reduced at 8,000–20,000 ng/l. Damselflies (Odonates) were reduced at 14,000 ng/l in the mesocosms, but were unaffected in the microcosms even at the highest treatment level. Bluegill survival was reduced at 110,000 ng/l and above; total fish biomass was reduced at 45,000 ng/l; individual growth was not affected at any treatment level; and reproduction (measured in mesocosms only) was unaffected at the highest mesocosm treatment level (28,000 ng/l). Plants and snails were not affected by any of the diazinon exposure levels tested.

The authors conclude that overall structure and function of the microcosm and mesocosm "ecosystems" did not appear to be affected at the lowest treatment levels of 2,300 to 5,000 ng/l, and that the Lowest Observable Adverse Effects Concentrations (LOAEC) for the microcosm and mesocosm "ecosystems" were 9,100 and 8,400 ng/l, respectively. The authors considered the LOAEC to be those at which effects were observed on major invertebrate groups.

However, certain individual species (cladocerans and some insects) were affected at concentrations as low as 2,300 ng/L, which is one-quarter the LOAEC for the micro/mesocosm "ecosystems". The authors do not report NOECs. The 2,300 ng/L concentration, at which effects were observed on certain sensitive species, was the lowest concentration tested. It is therefore not possible to determine the lowest concentration at which effects on sensitive species would begin. Presumably that concentration lies between 0 and 2,3000 ng/L, but without a value for the NOEC it is not possible to calculate an MATC that would be protective of sensitive species.

Literature Findings
A target or water quality objective could be derived from findings or studies presented in scientific journals. The most significant and potentially applicable findings are those by separate teams of British and American researchers on the impacts of diazinon to the olfactory function of Atlantic and Chinook salmon, respectively (Scholz et al., 2000, Moore and Waring, 1996). These studies have generally demonstrated effects at diazinon concentrations as low as 1,000 ng/L. The major water bodies for which targets are being considered in this report all have diazinon concentrations falling within the 0 to 1,000 ng/L diazinon range, although tributaries and drainage channels closer to the point of pesticide application can have concentrations well above 1,000 ng/L. Further study is needed to determine if impairments occur at concentrations between 0 and 1,000 ng/L of diazinon.

5.3 Comparison of Methods Used to Derive Numeric Targets

As shown above, a variety of methods exist for deriving numeric targets for the Sacramento River, San Joaquin River, and Delta. Table 6 contains a summary of the potential targets.

Table 6. Summary of Potential Targets

Method	Diazinon (ng/L)		Chlorpyrifos (ng/L)	
	Acute	Chronic	Acute	Chronic
Based on strict interpretation of Resolution 68-16 (Anti-Degradation Policy)	0	0	0	0
U.S. EPA Method as used by EPA	90	NA	83	41
U.S. EPA Method as used by CDFG	80	50	25	14
PERA Method	195 (5th percentile), 483 (10th percentile) (arthropods only)		NA	NA
Microcosm/mesocosm "ecosystem" LOEC	9,100 (microcosm) 8,400 (mesocosm)		NA	
Microcosm/mesocosm Cladoceran LOEC	<2,300		NA	
NA = Not Available				

Numeric Targets Based on Anti-degradation Policy

Numeric targets based on the Anti-degradation Policy would be highly protective of beneficial uses, and would be consistent with State and Federal Policies. They may also be difficult to achieve, and may be unnecessarily protective.

U.S. EPA Methodology as Used by U.S. EPA and CDFG

The U.S. EPA criteria method, as applied by U.S. EPA and CDFG, uses acute and chronic toxicity data for a wide range of species. Studies used to derive these data are screened to ensure compliance with accepted laboratory practices. Numbers obtained using this method are lower than levels known to be toxic to aquatic organisms, so the method is consistent with the established narrative toxicity objectives. The method has been used by the U.S. EPA for almost twenty years to establish water quality criteria, and has been supported by the CDFG since the late 1980s to assess hazards to aquatic organisms in the Sacramento-San Joaquin River and Delta.

The U.S. EPA criteria method is consistent with existing state and Federal regulations and Basin Plan provisions. The criteria are designed to be protective of the most sensitive aquatic organisms (invertebrates); the acute and chronic criteria are designed to avoid detrimental physiologic responses. National Pollutant Discharge Elimination System (NPDES) permit effluent limits are set to meet water quality objectives based on U.S. EPA criteria; using the same type of criteria to regulate non-point sources would be consistent with point source controls.

PERA Method as Applied to the Sacramento-San Joaquin River System

The PERA methodology as applied to the Sacramento-San Joaquin River system cited above (Giddings et al., 2000), is based on the assumption that some portion of individuals or species can be lost without significant damage to the ecosystem. The basis for this assumption is not clearly supported. Application of an approach that assumes lethality to a certain percentage of species could lead to the extirpation of sensitive species. This extirpation of sensitive species may place the ecosystem at greater risk in times when the remaining species are under environmental stress and a readjustment in balance takes place. The final balance in the ecosystem over the long term would not be known, and therefore it could not be concluded that beneficial uses were being protected as required by State policy in the Water Quality Control Plan. Such a conclusion would be especially applicable to the San Joaquin River system that is presently over-appropriated and subject to a number of other environmental stressors due to low flow conditions.

In addition, the PERA methodology is based on LC_{50} acute toxicity values, which means that the concentration associated with the tenth percentile of LC_{50} data does not protect 90% of species because the LC_{50} endpoint already represents 50% mortality of individuals. A significant number of individuals of several species will be impacted even at levels below the LC_{50} concentration. Therefore, at the proposed level of protection in the cited PERA example, detrimental physiological responses will occur significantly more than 10% of the time to significantly greater than 10% of the aquatic species (Marshack, 2000). This would be inconsistent with present State policy as defined in the Basin Plan's narrative objective of no toxicity.

While the U.S. EPA Office of Pesticide Programs has been involved in recent efforts to develop the PERA methodology, the method is still under development and is not currently being used by the U.S. EPA Office of Water to establish water quality criteria.

It is possible that the PERA methodology could be applied in a manner consistent with protection of the most sensitive species. One alternative would be to apply an appropriate safety factor to the 5^{th} (or lower) percentile of the LC_{50} acute toxicity values for arthropods, thereby increasing the percent of species protected and accounting for acute effects that occur below the LC_{50} concentration. Additionally, the application of the PERA methodology would need to be modified to account for chronic effects. If sufficient data were available, this could be done by developing a probability distribution of NOECs or LOECs and applying an appropriate safety factor to the 5^{th} (or lower) percentile of the NOECs or LOECs.

Microcosm and Mesocosm Studies

Microcosms and mesocosms do not necessarily mimic actual environmental conditions with respect to the aqueous chemistry of the constituents, or in terms of organism exposure in the test system. The microcosm/mesocosm studies cited above (Giddings et al., 1996; Giddings, 1992) did not report an NOEC and therefore it is not possible to determine what concentration would result in no impacts to sensitive species, such as cladocerans. The authors view cladocerans and other “numerically minor insect taxa” as not ecologically important, but these species are food for many fish, including salmonids. In addition, the premise that some species do not need to be protected is not consistent with State policy as defined in the Basin Plan’s narrative toxicity objective and the definition for the freshwater habitat beneficial uses.

5.4 Recommended Target

The numeric targets selected by the Regional Board will be adopted as a WQO. Therefore, the recommended target must comply with the following evaluation criteria:

1. protects beneficial uses, including preservation or enhancement of aquatic habitat, including invertebrates
2. consistent with the interpretation of beneficial use protection contained in the existing narrative toxicity and pesticide objectives, i.e., does not allow detrimental physiological responses in aquatic life
3. consistent with Federal regulations, including requirements for establishment of water quality criteria. Numerical criteria must be based on “…(i) 304(a) Guidance; or (ii) 304(a) Guidance modified to reflect site-specific conditions; or (iii) other scientifically defensible methods” (40 CFR § 131.11 (b) et seq.).

The selected method must be consistent with State policy to be acceptable to the SWRCB, the Office of Administrative Law, and the U.S. EPA, all of whom must ultimately approve the WQOs.

A target established based on the anti-degradation provision alone could result in a target established at natural background levels, which would be “zero”. Such a target would meet all three evaluation criteria since it protects beneficial uses, would not result in detrimental physiological responses, and is consistent with State and Federal regulations.

As currently applied, the PERA method does not appear to meet the above evaluation factors, since concentrations of diazinon at lethal levels are accepted for a certain percentage of species. This is in conflict with the narrative toxicity objective, which does not allow detrimental physiological responses in aquatic life. The defined beneficial use, which includes preservation or enhancement of invertebrates, would not appear to be protected. The PERA method is not described in 304(a) guidance, nor is it a site-specific modification of that guidance. PERA may be scientifically defensible as a methodology to derive water quality criteria if different risk assumptions were used.

The microcosm/mesocosm studies presented here did not report an NOEC and therefore it is not possible to determine what concentration would result in no impacts to sensitive species, such as cladocerans. The authors view cladocerans and other “numerically minor insect taxa” as not ecologically important. The freshwater habitat beneficial use definitions do not make distinctions between different species or taxa, so the study results do not appear to be consistent with full protection of beneficial uses. The allowance of detrimental physiological responses in aquatic life is also inconsistent with the interpretation of beneficial use protection contained in existing narrative toxicity objectives. The microcosm/mesocosm studies could serve as a "scientifically defensible method" for purposes of water quality criteria derivation, if the studies were found to reflect environmental conditions in the Central Valley and if different assumptions were made regarding effects of concern.

The CDFG Hazard Assessment criteria, which use U.S. EPA's methodology, is designed to protect all the aquatic life species and the methods would, therefore, appear to meet all the evaluation factors. The CDFG criteria are intended to avoid detrimental physiological responses and are based on the EPA's 304(a) guidance.

Based on information currently available to Regional Board staff, it appears an acceptable diazinon target would be between "zero" and the target derived by CDFG: 50 ng/L 4-day average and 80 ng/L 1-hour average. An acceptable chlorpyrifos target would be between "zero" and the target derived by CDFG: 14 ng/L 4-day average and 25 ng/L 1-hour average.

Establishment of the final numeric targets and WQOs, however, will also depend on the evaluation of a number of factors. These factors include: the environmental characteristics of the watershed; water quality conditions that could be reasonably achieved through the coordinated control of all factors which affect water quality in the area; economic considerations; the need for developing housing in the region; and the need to develop and use recycled water (§13241; Porter-Cologne Water Quality Act).

Future scientific findings on the aquatic toxicity of diazinon or chlorpyrifos may also affect the numeric targets. In addition, the need to protect sensitive native or resident organisms, such as endangered species, may necessitate lower numeric targets.

Attainability of the targets, together with the other factors listed, will be evaluated as an implementation program for the TMDL is developed. Based solely on consideration of protection of beneficial uses and the information currently available to Board staff, it appears an acceptable target would be between "zero" and the diazinon and chlorpyrifos targets derived by the California Department of Fish and Game. These targets would apply only in the main stem rivers and main channels of the Delta.

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